Dalton
Transactions

RSC Publishing

PAPER

View Article Online
View Journal | View Issue

Cite this: *Dalton Trans.*, 2013, **42**, 15183

Oxa-thia-, oxa-selena and crown ether macrocyclic complexes of tin(II) tetrafluoroborate and hexafluorophosphate – synthesis, properties and structures†

Christopher Beattie, Paolo Farina, William Levason* and Gillian Reid

The reactions of $Sn(BF_4)_2$ and $Sn(PF_6)_2$ with crown ethers and oxa-thia- or oxa-selena-macrocycles are complex, with examples of fragmentation of the fluoroanions, and cleavage of the ligands observed, in addition to adduct formation. The reaction of $Sn(BF_4)_2$ with 15-crown-5 or 18-crown-6 produced the sandwich complex [Sn(15-crown-5)$_2$][BF$_4$]$_2$ with 10-coordinate tin, and [Sn(18-crown-6)(H$_2$O)][BF$_4$]$_2$·2H$_2$O which has an hexagonal pyramidal tin centre with two long contacts to lattice water molecules (overall 7 + 2 coordination). [Sn(18-crown-6)(PF$_6$)][PF$_6$] is formed from 18-crown-6 and $Sn(PF_6)_2$, but the hexafluorophosphate ions hydrolyse readily in these systems to produce F^- which coordinates to the tin to produce [Sn(18-crown-6)F][PF$_6$], which can also be made directly from $Sn(PF_6)_2$, 18-crown-6 and KF in MeCN. The structure contains a hexagonal pyramidal coordinated Sn(II) cation with an apical fluoride. The oxa-thia macrocycle [18]aneO$_4$S$_2$ forms [Sn([18]aneO$_4$S$_2$)(H$_2$O)$_2$(PF$_6$)][PF$_6$], from which some crystals of composition [Sn([18]aneO$_4$S$_2$)(H$_2$O)$_2$(PF$_6$)]$_2$[PF$_6$][F] were obtained. The cation contains an approximately planar O$_4$S$_2$ coordinated macrocycle, with two coordinated water molecules on one side of the plane and a weakly bound (κ^2) PF_6^- group on the opposite face, and with the fluoride ion hydrogen bonded to the coordinated water molecules. In contrast, the oxa-selena macrocycle, [18]aneO$_4$Se$_2$, produces an anhydrous complex [Sn([18]aneO$_4$Se$_2$)(PF$_6$)$_2$] which probably contains coordinated anions, although it decomposes quite rapidly in solution, depositing elemental Se, and hence crystals for an X-ray study were not obtained. Reacting $Sn(BF_4)_2$ and [18]aneO$_4$Se$_2$ or [18]aneO$_4$S$_2$ also causes rapid decomposition, but from the latter reaction crystals of the 1,2-ethanediol complex [Sn([18]aneO$_4$S$_2$)-{C$_2$H$_4$(OH)$_2$}][BF$_4$]$_2$ were isolated. The structure reveals the coordinated macrocycle and a chelating diol, with the O–H protons of the latter hydrogen bonded to the $[BF_4]^-$ anions. This is a very rare, structurally authenticated example of ring opening/cleavage of an oxa-thia macrocycle. The new complexes were characterised by microanalysis, IR, ^{1}H, ^{19}F{^{1}H} and ^{31}P{^{1}H} NMR spectroscopy as appropriate, and X-ray structures are reported for [Sn(15-crown-5)$_2$][BF$_4$]$_3$[H$_3$O]·H$_2$O, [Sn(18-crown-6)(H$_2$O)][BF$_4$]$_2$·2H$_2$O, [Sn(18-crown-6)F][PF$_6$], [Sn([18]aneO$_4$S$_2$)(H$_2$O)$_2$(PF$_6$)]$_2$[PF$_6$][F] and [Sn([18]aneO$_4$S$_2$){C$_2$H$_4$(OH)$_2$}][BF$_4$]$_2$. The complexes are compared and contrasted with chloro-tin(II) complexes of crown ethers, germanium(II) and lead(II) analogues.

Received 12th July 2013,
Accepted 19th August 2013

DOI: 10.1039/c3dt51889b

www.rsc.org/dalton

Introduction

Studies of crown ether coordination chemistry initially focused on s- and f-block metals,[1] but more recently have played a significant role in developing the chemistry of p-block metals and metalloids.[2] Mixed O/S macrocycles (oxa-thia crowns) significantly extend the range of coordination properties, as do the little studied oxa-selena macrocycles.[3] Within Group 14, recent work has reported *endocyclic* germanium(II) crown[4,5] and oxa-thia crown[6] complexes, whereas thia- and selena-crown adducts contain *exocyclic* ligands and are polymeric.[6,7] Lead(II) oxo-salts, including nitrate, acetate or perchlorate, coordinate to crown ethers and thia crowns to produce complexes with high coordination numbers (8–11) and irregular geometries, all containing *endocyclic* crowns.[8–13] We recently reported complexes of crown ethers, oxa-thia and oxa-selena crowns with $Pb(BF_4)_2$ and $Pb(PF_6)_2$, which also gave a range of high-coordination number complexes with *endocyclic* ligands,

---

School of Chemistry, University of Southampton, Southampton SO17 1BJ, UK. E-mail: wxl@soton.ac.uk

†Electronic supplementary information (ESI) available. CCDC 949204–949208. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt51889b

but unexpectedly, these often incorporated coordinated fluoroanions, and the usually stable $[PF_6]^-$ anions in these complexes were readily hydrolysed in solution.[14]

The intermediate metal, tin has also attracted recent attention. Crown ether complexes with Sn(II) chloride include $[Sn(15\text{-crown-}5)_2][SnCl_3]_2$ which has a sandwich structure with the tin in an irregular 10-coordinate environment, and [Sn(18-crown-6)Cl][Y] (Y = $SnCl_3$ or ClO_4) with hexagonal pyramidal tin cations.[15–18] Recently, complexes with tin(II) triflate have been reported, $[Sn(18\text{-crown-}6)(O_3SCF_3)][O_3SCF_3]$ and $[Sn(15\text{-crown-}5)_2][O_3SCF_3]_2$, which have similar structures to the chlorostannate(II) complexes.[19,20] The Sn–O bond lengths within the cations vary widely, although computational studies have suggested that the tin-based lone pair is predominantly in the 5s orbital and therefore not primarily responsible for the distorted geometries. DFT calculations, ^{119}Sn Mössbauer and SSNMR studies suggest significant differences between the Sn–Cl and Sn–O_3SCF_3 bonds. Complexes of tin(IV) halides with crown ethers and thia crowns have also been structurally characterised.[21,22]

Here we report the synthesis, structures and properties of complexes of crown ether, oxa-thia and oxa-selena crowns‡ with $Sn(BF_4)_2$ and $Sn(PF_6)_2$, which show that the anions present play a significant role in the chemistry observed, and that with heavier and softer donor ligands a range of structural motifs occur. Examples of cleavage of the oxa-thia and oxa-selena-macrocycles are also described.

Results and discussion

In contrast to lead, for which only divalent metal complexes are formed, tin has extensive chemistries of both Sn(II) and Sn(IV), and switches between the oxidation states quite readily.[2] The tin(II) reagents used in the present study were aqueous solutions of $Sn(BF_4)_2$ and $Sn(PF_6)_2$; neither is available in solid form, hence both were prepared *in situ* as required.

Tin(II) solutions are dioxygen sensitive, being readily oxidised to Sn(IV) and are also subject to pH-dependent hydrolysis, forming oligomeric hydroxo-bridged species at medium pH.[23] Previous studies of aqueous Sn(II) solutions have used $Sn(ClO_4)_2$ made from $Cu(ClO_4)_2$ and tin powder,[23] and nitromethane or liquid SO_2 solutions of $Sn(SbF_6)_2$[24] have been used for *in situ* ^{31}P and ^{119}Sn NMR spectroscopic studies of complex formation by polydentate phosphines.[25] In the present work solutions of $Sn(BF_4)_2$ were obtained by stirring an aqueous solution of $Cu(BF_4)_2$ with excess of tin powder under dinitrogen, and $Sn(PF_6)_2$ from excess SnO with aqueous HPF_6 (Experimental section). The *freshly prepared* solutions were characterised by ^{119}Sn NMR spectroscopy which showed singlets at $\delta = -901$ (BF_4) or -866 (PF_6), and in the ^{19}F NMR spectra only $[BF_4]^-$ or $[PF_6]^-$ were evident. The $Sn(BF_4)_2$ solution is stable for some days if protected from air, but the $Sn(PF_6)_2$ shows significant hydrolysis in a few hours, depositing a white precipitate and generating F^-, $[PO_2F_2]^-$ and $[PO_3F]^{2-}$. Solutions were made freshly and used immediately for synthesis of the macrocycle complexes.

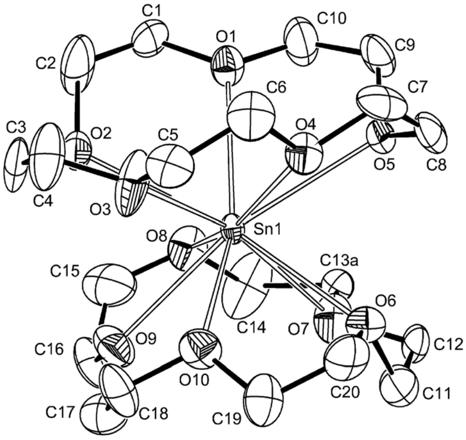

Fig. 1 The structure of the Sn containing cation in $[Sn(15\text{-crown-}5)_2][BF_4]_3[H_3O]\cdot H_2O$ showing the atom labelling scheme. The displacement ellipsoids are drawn at the 40% probability level and H atoms are omitted for clarity. For the disorder at C13 (modelled as two sites A/B) only the major component C13A is shown. Selected bond lengths (Å): Sn1–O3 = 2.589(5), Sn1–O10 = 2.621(5), Sn1–O9 = 2.676(5), Sn1–O4 = 2.678(5), Sn1–O6 = 2.726(6), Sn1–O5 = 2.742(5), Sn1–O7 = 2.747(6), Sn1–O1 = 2.752(5), Sn1–O2 = 2.771(5), Sn1–O8 = 2.856(5).

The reaction of $Sn(BF_4)_2$ with 15-crown-5 in H_2O–MeCN afforded poor yields of§ $[Sn(15\text{-crown-}5)_2][BF_4]_2$, which has the same cation as in $[Sn(15\text{-crown-}5)_2][CF_3SO_3]_2$[20] and $[Sn(15\text{-crown-}5)_2][SnCl_3]_2$.[19] Crystals grown from evaporation of a solution of the complex in wet MeCN proved upon structure solution to be $[Sn(15\text{-crown-}5)_2][BF_4]_3[H_3O]\cdot H_2O$ (Fig. 1), which were isomorphous with the lead(II) complex, $[Pb(15\text{-crown-}5)_2][BF_4]_3[H_3O]$,[14] although, the latter has badly disordered crown ligands. The Sn(II) complex has generally better defined ligands, with a range of Sn–O distances similar to those reported previously in the salts of different anions.[19,20] Thus 15-crown-5 forms a sandwich structured 10-coordinate tin cation, irrespective of the anions present.

Aqueous $Sn(BF_4)_2$ with 18-crown-6 in H_2O–MeCN afforded $[Sn(18\text{-crown-}6)(H_2O)][BF_4]_2\cdot 2H_2O$. The structure (Fig. 2) reveals the tin in a distorted hexagonal pyramidal geometry, with *endodentate* coordination to all six oxygens of the crown in a rather irregular manner (Sn–O = 2.537(8)–2.984(9) Å) with an apical water molecule (Sn–OH_2 = 2.150(7) Å), and with the tin below the basal plane. Two further water molecules make long contacts to the tin on the open face (Sn⋯OH_2 = 3.396(8), 3.304(9) Å). In [Sn(18-crown-6)Cl][Y] (Y = $SnCl_3$ or ClO_4) a chloride ligand occupies the apical site,[17] whilst in $[Sn(18\text{-crown-}6)(O_3SCF_3)][O_3SCF_3]$ a κ^1-triflate is present.[19] The lead(II) complex is quite different,[14] showing two pyramidal Pb(18-crown-6)(H_2O) units bridged by BF_4^- groups; [Pb(18-crown-6)-

---

‡$[18]aneO_4S_2$ = 1,4,10,13-tetraoxa-7,16-dithiacyclooctadecane, $[18]aneO_4Se_2$ = 1,4,10,13-tetraoxa-7,16-diselenacyclooctadecane.

§The low yields are those of isolated pure solids, substantial amounts of oily materials were produced on further concentration of the solutions.

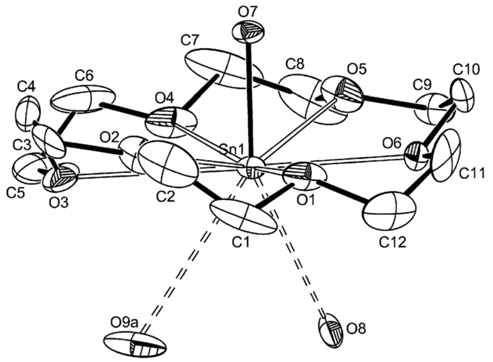

Fig. 2 The structure of the cation in [Sn(18-crown-6)(H_2O)][BF_4]$_2$·2H_2O showing the atom labelling scheme. The displacement ellipsoids are drawn at the 30% probability level and H atoms are omitted for clarity. The contacts to O8 and O9 are shown with dashed bonds. Symmetry operation: a = 1/2 + *x*, 1/2 − *y*, 1 − *z*. Selected bond lengths (Å) and angles (°): Sn1–O7 = 2.150(7), Sn1–O1 = 2.537(8), Sn1–O6 = 2.604(9), Sn1–O5 = 2.607(9), Sn1–O2 = 2.641(8), Sn1–O4 = 2.777(8), Sn1–O3 = 2.984(9), Sn1–O8 = 3.396(8), Sn1–O9 = 3.304(9), O7–Sn1–O1 = 82.3(3), O7–Sn1–O6 = 85.7(3), O7–Sn1–O5 = 74.5(3), O7–Sn1–O2 = 76.1(3), O7–Sn1–O2 = 76.1(3), O7–Sn1–O3 = 93.1(3), O1–Sn1–O6 = 62.7(4), O6–Sn1–O5 = 62.7(4), O1–Sn1–O2 = 60.8(3), O5–Sn1–O4 = 61.3(3), O2–Sn1–O3 = 55.9(3), O4–Sn1–O3 = 57.8(3).

(H_2O)}$_2$(μ-BF_4)$_2$][BF_4]$_2$. Spectroscopic and microanalytical data on the bulk solid are also consistent with the composition [Sn(18-crown-6)(H_2O)][BF_4]$_2$·2H_2O, and in MeCN solution ^{19}F NMR spectroscopy shows only ionic [BF_4]$^-$ groups are present. The complexes are generally rather poorly soluble in non- or weakly-coordinating solvents like halocarbons. Attempts to obtain a ^{119}Sn NMR spectrum of this complex in MeCN solution were unsuccessful, presumably due to dynamic exchange processes (this was true of all the crown complexes described), a problem encountered by others for tin-crowns[19,21] and in lead-crown complexes.[14]

Rather unexpectedly, the reaction of Sn(PF_6)$_2$ with 18-crown-6 in H_2O–MeOH solution gave a white powder, with the composition [Sn(18-crown-6)][PF_6]$_2$; both the microanalysis and the IR spectrum confirming the absence of water. The coordination sphere of the tin is thus likely to contain one or both PF_6^- groups, similar to that found in some of the lead(II) complexes.[14] In the IR spectrum of [Sn(18-crown-6)][PF_6]$_2$, the PF_6^- stretching mode at ~842 cm^{-1} was very broad and there were two bands in the PF_6^- bending region, which is consistent with some anion coordination, probably suggesting a [Sn(18-crown-6)(PF_6)][PF_6] constitution. On standing, the reaction solution produced a small number of colourless crystals, which were found to be [Sn(18-crown-6)F][PF_6], containing a coordinated fluoride in the apical position (Fig. 3). The fluoride clearly comes from degradation of the [PF_6]$^-$ and its presence is confirmed by a ^{19}F NMR resonance at $\delta = -96.5$, which is similar to those in SnF_2 adducts with oxygen donor ligands.[26] The complex can be synthesised directly from Sn(PF_6)$_2$, 18-crown-6 and KF in MeCN–H_2O. The structure of [Sn(18-crown-6)F][PF_6] (Fig. 3) shows a hexagonal pyramidal cation geometry similar to that in found [Sn(18-crown-6)Cl]$^+$,[17] and the Sn–O$_{crown}$ distances are very similar. Few complexes derived from SnF_2 are known,[26] but the Sn–F distance of 1.947(4) Å in the present complex is slightly shorter than those in [Sn(bipy)F]$^+$, [Sn(phen)F]$^+$ or [SnF_2(dmso)], which are ~2.02–2.03 Å.[26] There is no coordination of the PF_6^- groups and the packing diagram (see ESI†) shows interaction of the Sn(II) centre with a crown ether oxygen from a neighbouring molecule at ~3.62 Å which is close to the sum of the van der Waals radii (3.7 Å).[27]

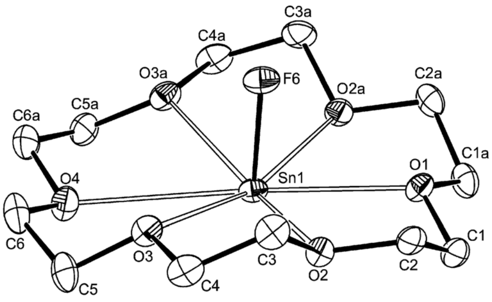

Fig. 3 The structure of the cation in [Sn(18-crown-6)F][PF_6], showing the atom labelling scheme. The displacement ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Bonds to Sn1 from the crown O atoms are shown as open bonds. Symmetry operation: a = −*x*, *y*, *z*. Selected bond lengths (Å) and angles (°): Sn1–F6 = 1.947(4), Sn1–O1 = 2.597(5), Sn1–O2 = 2.606(3), Sn1–O3 = 2.731(3), Sn1–O4 = 2.953(5), F6–Sn1–O1 = 83.16(17), F6–Sn1–O2 = 84.15(10), F6–Sn1–O3 = 83.20(17), F6–Sn1–O4 = 100.21(16), O1–Sn1–O2 = 62.69(7), O2–Sn1–O3 = 61.03(10, O3–Sn1–O4 = 57.77(10).

We were unable to isolate a pure complex from reaction of SnF_2 and 18-crown-6 in methanol, the *in situ* ^{19}F NMR spectra of the reaction solutions showed several species present, and the solids isolated on work up were clearly mixtures.

The reactions of the tin(II) fluoroanion salts with oxa-thia and oxa-selena macrocycles proved to be more difficult to unravel, and included some reactions in which the macrocyclic ring was cleaved. The reaction of Sn(PF_6)$_2$ with [18]aneO_4S_2 in MeCN–H_2O gave a white solid, identified by microanalysis and spectroscopically as [Sn([18]aneO_4S_2)(H_2O)$_2$(PF_6)][PF_6]. Colourless crystals grown from the mother liquor were found by X-ray structure determination to be [Sn([18]aneO_4S_2)(H_2O)$_2$-(PF_6)$_2$]$_2$[PF_6][F] (Fig. 4). The tin cation is coordinated to all six donor atoms of the oxa-thia crown (O_4S_2) and to two water molecules, giving eight-coordinate tin, with long contacts to two fluorines of a [PF_6]$^-$ group which lies on the opposite side of the Sn-macrocycle plane to the water molecules. The fluoride ion is hydrogen bonded to the coordinated water molecules, although the occupancy of the site is only 60%. The bond lengths are unexceptional, but the structure confirms the geometry of the cation. The unexpected incorporation of F$^-$ in place of a [PF_6]$^-$ group shows again the easy degradation of the hexafluorophosphate unit in these systems. The structure of the cation is similar to that observed previously[14] in [Pb(18-crown-6)(H_2O)$_2$(PF_6)][PF_6]·H_2O, with the fluoride ion replacing the lattice water molecule present in the lead complex.

In the previous work on Pb(II) complexes[14] and in the results reported above with Sn(II), the tetrafluoroborate systems were generally more robust than the rather easily decomposed

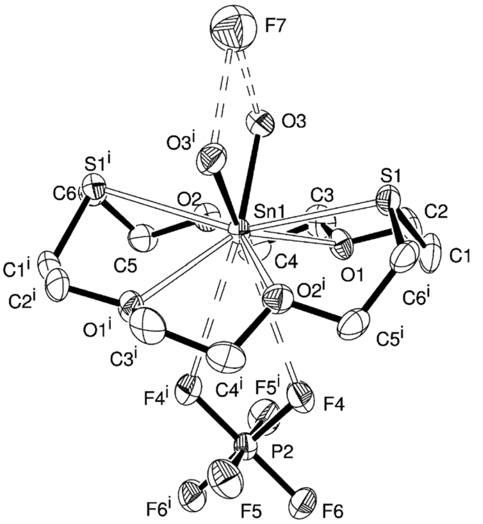

Fig. 4 The structure of the cation in $[Sn([18]aneO_4S_2)(H_2O)_2(PF_6)]_2[PF_6][F]$ showing the cation, an interacting $[PF_6]$ anion, the hydrogen bonding to the [F] anion and giving the labelling scheme. The displacement ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. The $[PF_6]$ anion which has contacts to Sn1 is also shown with dotted bonds for the two long Sn1⋯F4 distances. The atom site occupancy for F7 is 0.61. The molecule has 2-fold symmetry. Symmetry operation: a = $y + 1/2$, $x - 1/2$, y, $3/2 - z$. Selected bond lengths (Å) and angles (°): Sn1–O3 = 2.282(3), Sn1–O1 = 2.833(3), Sn1–O2 = 2.840(3), Sn1–S1 = 2.9787(10), Sn1–F4 = 3.485(3), O3–Sn1–O3a = 78.32(18), O3–Sn1–O3 = 78.32(18), O3–Sn1–O2 = 66.83(11), O3–Sn1–O2 = 66.83(11), O1–Sn1–S1 = 65.32(7), O1–Sn1–O2 = 60.45(9).

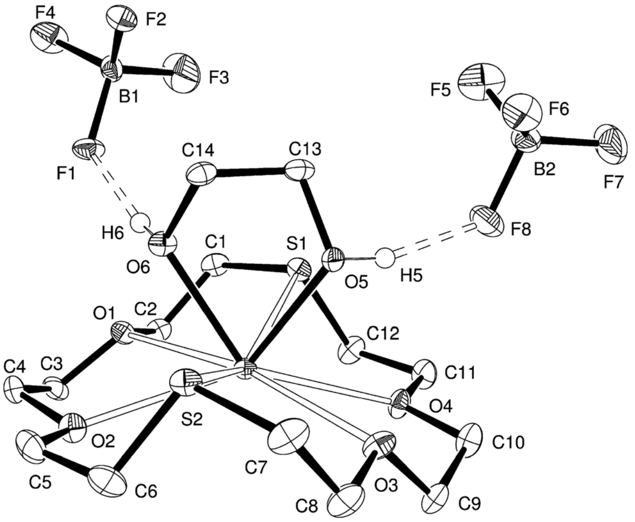

Fig. 5 The structure of $[Sn([18]aneO_4S_2)\{C_2H_4(OH)_2\}][BF_4]_2$ showing the hydrogen bonding to the $[BF_4]$ anions and the atom labelling scheme. The displacement ellipsoids are drawn at the 50% probability level and uninteracting H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Sn1–O5 = 2.340(2), Sn1–O6 = 2.346(2), Sn1–O4 = 2.727(2), Sn1–O3 = 2.812(2), Sn1–O2 = 2.820(2), Sn1–O1 = 2.892(2), Sn1–S2 = 2.9068(10), Sn1–S1 = 2.9659(9), O5–Sn1–O6 = 69.20(7), O3–Sn1–S2 = 66.98(5), O5–Sn1–O6 = 69.20(7), O4–Sn1–O3 = 59.94(7), O5–Sn1–O4 = 77.91(7), O2–Sn1–O1 = 60.15(6), O2–Sn1–S2 = 65.28(5).

hexafluorophosphate salts. It was thus surprising that repeated attempts to isolate a complex of $[18]aneO_4S_2$ with $Sn(BF_4)_2$ in aqueous MeCN or MeOH were unsuccessful. Typically, sticky white oils were obtained on work up, whose IR and ^{19}F NMR spectra showed the presence of organic species, anion and water, whilst the ^1H NMR spectra were unexpectedly complex, varying from batch to batch. Attempts to recrystallise the oils from MeOH or MeCN usually resulted in decomposition and the formation of grey-black solids. On occasion a few crystals were obtained from MeCN or MeOH solution, some of which were identified by unit cell determination as $[18]aneO_4S_2$. From one reaction the crystals isolated had the structure shown in Fig. 5. The composition is revealed as $[Sn([18]aneO_4S_2)\{C_2H_4(OH)_2\}][BF_4]_2$ with the tin coordinated to all the donors of the macrocycle and to a chelating 1,2-ethanediol ligand. The O–H protons of the latter were identified in the electron density map, and are hydrogen bonded to the $[BF_4]^-$ groups. The origin of the 1,2-ethanediol can only be from C–O bond cleavage of the oxa-thia macrocycle, and this appears to be the first time such degradation has been observed. Cleavage of C–S bonds in thia macrocycles by Re(II) or Tc(II) has been explored in some detail,[28,29] and $[Rh([9]aneS_3)_2]^{3+}$ can be deprotonated at the α-C, resulting in ring-opening to form a vinyl thioether.[30] ^1H NMR spectra of all the crude products from the various attempts at this reaction showed $[Sn([18]aneO_4S_2)\{C_2H_4(OH)_2\}]^{2+}$ present, although crystals were obtained on only the one occasion. The crystal structure shows that cleavage of the $[18]aneO_4S_2$ is occurring in these reactions, and partially accounts for the complexity of the ^1H NMR spectra (the other products have not been identified).

Attempts to isolate a complex of $[18]aneO_4Se_2$ with $Sn(BF_4)_2$ in MeCN–H_2O or MeOH–H_2O were similarly unsuccessful, the white solids formed initially rapidly deposited red selenium. However, using $Sn(PF_6)_2$, a white powder $[Sn([18]aneO_4Se_2)(PF_6)_2]$ was isolated. The IR spectrum confirms the absence of water, and the presence of single rather sharp features at 840 and 568 cm^{-1} suggesting only a single PF_6^- environment is present (see above). The ^{19}F and ^{31}P NMR spectra obtained from freshly prepared solutions showed no significant degradation of the anions and the ^1H NMR spectrum was typical of coordinated oxa-selena crown. However, upon standing MeOH or MeCN solutions darkened and deposited red selenium, and showed evidence of hydrolysis of the anion. This instability, combined with the modest solubility of the complex, prevented a ^{77}Se NMR spectrum being obtained. The instability also prevented crystal growth for a structure determination, but we note that Pb(II) forms $[Pb([18]aneO_4Se_2)(PF_6)_2]$, which contains a folded macrocycle and two κ^2-PF_6^- groups giving 10-coordinate lead,[14] and it seems likely that a similar structure is present in the Sn(II) complex.

Conclusions

The complexes of tin(II) tetrafluoroborate or hexafluorophosphate with these chalcogenoether macrocycles show considerable similarities to their Pb(II) analogues,[14] including *endo*-coordinated macrocycles with rather irregular metal geometries and high coordination numbers (8–10). For both the Sn(II) and Pb(II) systems, the hexafluorophosphate anion proves to be surprisingly readily hydrolysed, and in the Sn(II) case, the liberated fluoride may end up coordinated, as in [Sn(18-crown-6)F][PF_6]. The tin(II) complexes are less robust than their Pb(II) analogues, for example in the rapid cleavage of [18]aneO_4Se_2 with elimination of elemental Se, and in the C–O cleavage and ring-opening in the [18]aneO_4S_2 systems. It is possible that the higher charge/radius ratio in the tin (covalent radii Sn(II): 1.39; Pb(II): 1.46 Å)[27] makes the tin more polarising and promotes bond breaking. Although tin differs from lead in having an accessible higher oxidation state, we saw no evidence for any Sn(IV) formation in these systems. Comparisons of the structural data on crown and oxa-thia crown complexes of Ge(II), Sn(II) and Pb(II)[4–6,14,17,18] reveal irregular coordination of the macrocycles and a range of M–O/S distances. An extreme case is [Ge([18]aneS_3O_3)Cl][$GeCl_3$] where only five donors (S_2O_3) are coordinated to the small germanium, but even for the larger Sn(II) in the present work a surprisingly wide range of distances are found, for example in [Sn(15-crown-5)$_2$][BF_4]$_3$[H_3O]·H_2O, the Sn–O distances range from 2.589(5) to 2.856(5) Å, which suggests that the potential wells about the tin are quite shallow. For the 18-membered ring complexes with anion or water coordination to the tin or lead, examples have been described above of intermolecular interactions, hydrogen-bonding between coordinated water and lattice water or the anions present, and all of these will affect the detailed geometries observed.

Experimental

Infrared spectra were recorded as Nujol mulls between CsI plates using a Perkin-Elmer Spectrum100 spectrometer over the range 4000–200 cm^{-1}. ^1H NMR spectra were recorded using a Bruker AV300 spectrometer. $^{19}F\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were obtained on a Bruker DPX400 and are referenced to $CFCl_3$ and H_3PO_4 respectively. ^{119}Sn NMR spectra were obtained on a Bruker DPX400 and referenced to Me_4Sn. ^{119}Sn spectra were recorded without proton decoupling and with a 3 s pulse delay. Microanalyses were undertaken by Medac Ltd or London Metropolitan University. Solvents were dried by distillation prior to use, CH_2Cl_2 and MeCN from CaH_2, and hexane from sodium benzophenone ketyl. 18-Crown-6 and 15-crown-5 were obtained from Aldrich and used as received. The ligands [18]aneO_4S_2 and [18]aneO_4Se_2 were made by literature methods.[14,31,32] All preparations were undertaken several times to ensure reproducibility.

Aqueous Sn(BF_4)$_2$ solution

Cu(BF_4)$_2$·6H_2O (2.324 g, 6.73 mol) was dried *in vacuo* at 40 °C for 2 h. Degassed water (60 mL) was added and an excess of Sn powder (0.821 g, 6.92 mol) was stirred in. The blue solution went colourless overnight and a black precipitate deposited. The solution was filtered, and the tin(II) concentration estimated from the amount of copper complex used, assuming complete conversion. The solution was used within a few days. $^{19}F\{^1H\}$ NMR (CD_3CN, 293 K): $\delta = -150.6$ (s). ^{119}Sn NMR (D_2O–H_2O, 293 K): $\delta = -901$ (s). The solution begins to deposit a black precipitate (possibly SnO) after around 7 days and decomposition of the [BF_4]$^-$ group can be observed by $^{19}F\{^1H\}$ NMR spectroscopy. It must be kept under N_2 at all times.

Aqueous Sn(PF_6)$_2$ solution

SnO (0.097 g, 7.20×10^{-4} mol) was suspended in degassed H_2O (4 mL), and HPF_6, as a 65% aqueous solution (0.210 g, 1.44×10^{-3} mol) was added slowly. Further SnO was added until no more dissolved. The solution was filtered and used immediately. $^{19}F\{^1H\}$ NMR (D_2O, 293 K): $\delta = -72.0$ (d, $^1J_{PF}$ = 710 Hz). $^{31}P\{^1H\}$ NMR (D_2O, 293 K): $\delta = -144.4$ (septet). ^{119}Sn NMR (D_2O, 293 K): $\delta = -866$ (s). The solution decomposes within 5 h, depositing a lot of white precipitate, both the $^{19}F\{^1H\}$ NMR and $^{31}P\{^1H\}$ NMR showing the relatively rapid hydrolysis of the [PF_6]$^-$ group upon standing.

[Sn(18-crown-6)(H_2O)][BF_4]$_2$·2H_2O

Aqueous Sn(BF_4)$_2$ (containing 0.08 g, 2.8×10^{-4} mol tin) was added dropwise to 18-crown-6 (0.072 g, 2.78×10^{-4} mol) in MeCN (20 mL) upon which a fine white solid precipitated out. The reaction mixture was left to stir at room temperature for 12 h. The suspension was concentrated, allowed to stand and then filtered. The white solid was then washed with CH_2Cl_2 and dried *in vacuo*. A few X-ray quality crystals were obtained by slow evaporation from the washings. Yield: 0.019 g, 12%. Required for $C_{12}H_{30}B_2F_8O_9Sn$ (610.89): C, 23.6; H, 5.0. Found: C, 23.4; H, 4.3%. IR (Nujol, cm^{-1}): 3528, 1640 (H_2O), 1095, 1029, 519 (BF_4). ^1H NMR (CD_2Cl_2, 298 K): $\delta = 3.84$ (s, crown C$\boldsymbol{H}_2$); (CD_3CN, 298 K): $\delta = 2.19$ (br, $\boldsymbol{H}_2$O), 3.78 (s, crown C$\boldsymbol{H}_2$). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 298 K): $\delta = -151.4$ (s).

[Sn(15-crown-5)$_2$][BF_4]$_2$

Aqueous Sn(BF_4)$_2$ (0.1 g, 3.33×10^{-4} mol) was added dropwise to 15-crown-5 (0.146 g, 6.63×10^{-4} mol) in MeCN (15 mL), upon which a fine white solid precipitated out. The reaction mixture was left to stir at room temperature for 2 h. The suspension was concentrated and then filtered. The white solid was then washed with CH_2Cl_2 and dried *in vacuo*. Yield: 0.018 g, 6%. Repeated syntheses of this complex gave poor isolated yields which are probably due to the difficulty of isolation of the solid complex rather than to other species present (see text). Required for $C_{20}H_{40}B_2F_8O_{10}Sn$ (732.96): C, 32.7; H, 5.5. Found: C, 32.6; H, 5.4%. IR (Nujol, cm^{-1}): 1084, 526 (BF_4). ^1H NMR (CD_3CN, 298 K): $\delta = 3.83$ (s, crown C$\boldsymbol{H}_2$). $^{19}F\{^1H\}$ NMR (CD_3CN, 298 K): $\delta = -151.2$ (s). X-Ray quality crystals were grown by redissolving the solid in MeCN and slow evaporation in air, and proved to be [Sn(15-crown-5)$_2$][BF_4]$_3$[H_3O]·H_2O (see Results and discussion).

[Sn(18-crown-6)][PF_6]$_2$

Aqueous Sn(PF_6)$_2$ (0.16 g, 3.90×10^{-4} mol) was added dropwise to 18-crown-6 (0.10 g, 3.90×10^{-4} mol) dissolved in MeOH (15 mL), and left to stir at room temperature for 24 h.

Table 1 Crystal data and structure refinement details[a]

Compound	$[Sn(15\text{-crown-}5)_2][BF_4]_3[H_3O]\cdot H_2O$	$[Sn(18\text{-crown-}6)(H_2O)][BF_4]_2\cdot 2H_2O$	$[Sn(18\text{-crown-}6)F][PF_6]$
Formula	$C_{20}H_{45}B_3F_{12}O_{12}Sn$	$C_{12}H_{30}B_2F_8O_9Sn$	$C_{12}H_{24}F_7O_6PSn$
M	856.68	610.67	546.97
Crystal system	Monoclinic	Orthorhombic	Orthorhombic
Space group (no.)	$P2_1/n$ (14)	$Pbca$ (61)	$Pmc2_1$ (26)
a/Å	14.116(2)	21.368(6)	10.676(4)
b/Å	15.118(2)	17.042(4)	10.498(4)
c/Å	16.137(6)	12.503(2)	8.533(3)
α/°	90	90	90
β/°	90.793(6)	90	90
γ/°	90	90	90
U/Å^3	3443.6(14)	4553.3(19)	956.4(6)
Z	4	8	2
μ (Mo-K$_\alpha$)/mm^{-1}	0.859	1.227	1.512
F(000)	1736	2448	544
Total number reflns	16 402	18 854	544
R_{int}	0.0295	0.1119	0.0460
Unique reflns	7805	4461	2302
No. of params, restraints	432, 2	289, 4	137, 1
R_1, wR_2 $[I > 2\sigma(I)]^b$	0.0730, 0.0913	0.0828, 0.1527	0.0381, 0.0432
R_1, wR_2 (all data)	0.1894, 0.2061	0.1916, 0.1916	0.0870, 0.0895

Compound	$[Sn([18]aneO_4S_2)(C_2H_4(OH)_2)][BF_4]_2$	$[Sn([18]aneO_4S_2)(H_2O)_2]_2[PF_6]_3F$
Formula	$C_{14}H_{30}B_2F_8O_6S_2Sn$	$C_{24}H_{56}F_{19}O_{12}P_3S_4Sn_2$
M	650.81	1356.22
Crystal system	Monoclinic	Tetragonal
Space group (no.)	$P2_1/c$ (14)	$P4/ncc$ (130)
a/Å	8.4182(15)	17.656(3)
b/Å	15.129(4)	17.656(3)
c/Å	19.264(7)	15.5791(10)
α/°	90	90
β/°	100.326(7)	90
γ/°	90	90
U/Å^3	2413.7(11)	4856.5(12)
Z	4	4
μ (Mo-K$_\alpha$)/mm^{-1}	1.321	1.421
F(000)	1304	2704
Total number reflns	27 195	54 421
R_{int}	0.0590	0.0551
Unique reflns	5512	2785
No. of params, restraints	305, 2	148, 0
R_1, wR_2 $[I > 2\sigma(I)]^b$	0.0346, 0.0551	0.0470, 0.0593
R_1, wR_2 (all data)	0.0682, 0.0735	0.1283, 0.1350

[a] Common items: temperature = 100 K; wavelength (Mo-K$_\alpha$) = 0.71073 Å; θ(max) = 27.5°. [b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; w$R_2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$.

The slightly turbid solution was filtered and the filtrate concentrated *in vacuo*. A small amount of white solid began to form; the mother liquor was left at 5 °C for 2 d. A large quantity of white solid was filtered off and dried. Yield: 0.10 g, 38%. Required for $C_{12}H_{24}F_{12}O_6P_2Sn$ (672.79): C, 21.4; H, 3.6. Found: C, 21.5; H, 3.5%. IR (Nujol, cm^{-1}): 841 (vbr), 559, 531 (PF_6). ^1H NMR (CD_3CN, 298 K): δ = 3.77 (s, crown C$\boldsymbol{H}_2$). $^{19}F\{^1H\}$ NMR (CD_3CN, 298 K): δ = −73.2 (d, $^1J_{PF}$ = 710 Hz, PF_6). $^{31}P\{^1H\}$ NMR (CD_3CN, 298 K): δ = −144.1 (septet).

[Sn(18-crown-6)F][PF$_6$]

[Sn(18-crown-6)][PF$_6$]$_2$ (0.037 g, 5.50 × 10^{-4} mol) and KF (0.003 g, 5.50 × 10^{-4} mol) were dissolved in MeCN (5 mL) and allowed to stir over 3 d. The reaction began to opalesce, the mother liquor was filtered and the volatiles allowed to evaporate. The crude white solid was taken up in MeCN, refiltered and a pure white solid was obtained on removal of the volatiles. Yield: 0.012 g, 39%. Required for $C_{12}H_{24}F_7O_6PSn$ (546.8): C, 26.3; H, 4.4. Found: C, 26.3; H, 4.6%. IR (Nujol, cm^{-1}): 835, 555 (PF_6). ^1H NMR (CD_3CN, 298 K): δ = 3.59 (s, crown C$\boldsymbol{H}_2$). $^{19}F\{^1H\}$ NMR (CD_3OH, 298 K): δ = −96.5, −73.2 (d, $^1J_{PF}$ = 710 Hz, PF_6). $^{31}P\{^1H\}$ NMR (CD_3CN, 298 K): δ = −144.7 (septet).

[Sn([18]aneO$_4$S$_2$)(H$_2$O)$_2$(PF$_6$)][PF$_6$]

Aqueous Sn(PF$_6$)$_2$ (0.16 g, 3.38 × 10^{-4} mol) was added dropwise to [18]aneO$_4$S$_2$ (0.100 g, 3.38 × 10^{-4} mol) dissolved in MeOH (15 mL). The reaction was left to stir at room temperature for 12 h, during which a minor amount of fine solid formed. The solution was filtered, concentrated to ~3 mL and cooled for 7 d at 5 °C. Large colourless crystals grew; these were filtered off and dried *in vacuo*. Yield: 0.056 g, 22%. Required for $C_{12}H_{28}F_{12}O_6P_2S_2Sn$ (740.77): C, 19.4; H, 3.8. Found: C, 19.6; H, 3.7%. IR (Nujol, cm^{-1}): 3397, 1635 (H_2O), 837, 557 (PF_6). ^1H NMR (CD_3CN, 298 K): δ = 2.88 (br, $\boldsymbol{H_2}O$), 3.02 (t, [8H], $SC\boldsymbol{H_2}$), 3.74 (s, [8H], $OC\boldsymbol{H_2}$), 3.83 (t, [8H], $SCH_2C\boldsymbol{H_2}O$). $^{19}F\{^1H\}$ NMR (CD_3CN, 298 K): δ = −72.3 (d, $^1J_{PF}$ = 710 Hz, PF_6). $^{31}P\{^1H\}$ NMR (CD_3CN, 298 K): δ = −143.3 (septet).

[Sn([18]aneO$_4$Se$_2$)(PF$_6$)$_2$]

Aqueous $Sn(PF_6)_2$ (0.10 g, 2.17 × 10^{-4} mol) was added dropwise to [18]aneO$_4$Se$_2$ (0.085 g, 2.17 × 10^{-4} mol) dissolved in dry MeOH (15 mL) and left to stir at room temperature for 4 h. The solution was filtered and concentrated to ~5 mL. The filtrate was cooled for 5 days at 5 °C. A substantial quantity of amorphous white solid formed, which was isolated and dried *in vacuo*. Yield: 0.066 g, 35%. Required for $C_{12}H_{24}F_{12}O_4P_2Se_2Sn$ (798.73): C, 18.0; H, 3.0. Found: C, 18.2; H, 3.1%. IR (Nujol, cm^{-1}): 840, 558 (PF_6). ^1H NMR (CD_3CN, 298 K): δ = 2.99 (t, [8H], $SeC\boldsymbol{H_2}$), 3.72 (s, [8H], $OC\boldsymbol{H_2}$), 3.84 (t, [8H], $SeCH_2C\boldsymbol{H_2}O$). $^{19}F\{^1H\}$ NMR (CD_3CN, 298 K): δ = −72.3 (d, $^1J_{PF}$ = 710 Hz, PF_6). $^{31}P\{^1H\}$ NMR (CD_3CN, 298 K): δ = −143.3 (septet).

X-Ray crystallography

Details of the crystallographic data collection and refinement parameters are given in Table 1. Crystals suitable for single crystal X-ray analysis were obtained as described above. Data collections used a Rigaku AFC12 goniometer equipped with an enhanced sensitivity (HG) Saturn724+ detector mounted at the window of an FR-E+ SuperBright molybdenum (λ = 0.71073 Å) rotating anode generator with VHF Varimax optics (100 µm focus) with the crystal held at 100 K (N_2 cryostream). Structure solution and refinement were straightforward,[33,34] except as detailed below, with H atoms bonded to C being placed in calculated positions using the default C–H distance. Hydrogen atoms attached to water molecules were not identified in the difference Fourier maps. They were inferred from the O⋯F and O⋯O distances. In $[Sn([18]aneO_4S_2)(H_2O)_2]_2[PF_6]_3F$ charge balance required the partial occupancy of fluoride ions over two sites. For $[Sn(15\text{-crown-}5)_2][BF_4]_3[H_3O]\cdot H_2O$, C13 was modelled as disordered over two sites A/B. For $[Sn(18\text{-crown-}6)(H_2O)][BF_4]_2\cdot 2H_2O$ the data were weak with very elongated ellipsoids for the C atoms. Attempts to model the ellipsoids as disordered carbon atoms was unsuccessful.

Acknowledgements

We thank EPSRC and the University of Southampton for support, and Dr M. Webster for assistance with the crystallographic data analyses.

References

1 R. D. Rodgers and C. B. Bauer, in *Comprehensive Supramolecular Chemistry*, ed. J. L. Atwood, J. E. D. Davies, D. D. MacNicol and F. Vogtle, Pergamon, Oxford, 1996, vol. 1, p. 315.
2 *Comprehensive Coordination Chemistry II*, ed. J. A. McCleverty and T. J. Meyer, Elsevier, Oxford, 2004, vol. 3.
3 W. Levason and G. Reid, in *Supramolecular Chemistry From Molecules to Nanomaterials*, ed. P. A. Gale and J. W. Steed, Wiley, NY, 2012, vol. 3, p. 785.
4 F. Cheng, A. L. Hector, W. Levason, G. Reid, M. Webster and W. Zhang, *Angew. Chem., Int. Ed.*, 2009, **48**, 5152.
5 P. A. Rupar, R. Bandyopadhyay, B. F. T. Cooper, M. R. Stinchcombe, P. Ragogna, C. L. B. MacDonald and K. M. Baines, *Angew. Chem., Int. Ed.*, 2009, **48**, 5155.
6 A. L. Hector, W. Levason, G. Reid, M. Webster and W. Zhang, *Dalton Trans.*, 2011, **40**, 694.
7 F. Cheng, A. L. Hector, W. Levason, G. Reid, M. Webster and W. Zhang, *Chem. Commun.*, 2008, 5508.
8 R. D. Rogers and A. M. Bond, *Inorg. Chim. Acta*, 1992, **192**, 167.
9 A. Y. Nazarenko and E. B. Rusanov, *Polyhedron*, 1994, **13**, 2549.
10 M. G. B. Drew, D. G. Nicholson, I. Sylte and A. K. Vasudevan, *Acta Chem. Scand.*, 1992, **46**, 396.
11 A. J. Blake, D. Fenske, W.-S. Li, V. Lippolis and M. Schröder, *J. Chem. Soc., Dalton Trans.*, 1998, 3961.
12 H.-J. Kuppers, K. Weighardt, B. Nuber and J. Weiss, *Z. Anorg. Allg. Chem.*, 1989, **577**, 155.
13 I.-H. Park, K.-M. Park and S. S. Lee, *Dalton Trans.*, 2010, **39**, 9696.
14 P. Farina, T. Latter, W. Levason and G. Reid, *Dalton Trans.*, 2013, **42**, 4714.
15 R. H. Herber and G. Carrasquillo, *Inorg. Chem.*, 1981, **20**, 3693.
16 R. H. Herber and A. E. Smelkinson, *Inorg. Chem.*, 1978, **17**, 1023.
17 M. G. B. Drew and D. G. Nicholson, *J. Chem. Soc., Dalton Trans.*, 1986, 1543.
18 E. Hough, D. G. Nicholson and A. K. Vasudevan, *J. Chem. Soc., Dalton Trans.*, 1989, 2155.
19 R. Bandyopadhyay, B. F. T. Cooper, A. J. Rossini, R. W. Schurko and C. L. B. MacDonald, *J. Organomet. Chem.*, 2010, **695**, 1012.
20 C. L. B. Macdonald, R. Bandyopadhyay, B. F. T. Cooper, W. W. Friedl, A. J. Rossini, R. W. Schurko, R. W. Eichhorn and R. H. Herber, *J. Am. Chem. Soc.*, 2012, **134**, 4332.
21 M. Schaefer and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 1992, **615**, 127; G. Bott, H. Prinz, A. Alvanipour and J. L. Atwood, *J. Coord. Chem.*, 1987, **16**, 303; P. A. Cusack, B. N. Patel and P. J. Smith, *Inorg. Chim. Acta*, 1983, **76**, L21.
22 W. Levason, M. L. Matthews, R. Patel, G. Reid and M. Webster, *New J. Chem.*, 2003, **27**, 1784; G. R. Willey, A. Jarvis, J. Palin and W. Errington, *J. Chem. Soc., Dalton Trans.*, 1994, 255; M. M. Olmstead, K. A. Williams and K. Musker, *J. Am. Chem. Soc.*, 1982, **104**, 5567.
23 S. Gobom, *Acta Chem. Scand., Ser. A*, 1976, **30**, 745; R. S. Tobias, *Acta Chem. Scand.*, 1958, **12**, 198.
24 A. J. Edwards and K. Khallow, *J. Chem. Soc., Chem. Commun.*, 1984, 50; T. Birchall, P. A. W. Dean and R. J. Gillespie, *J. Chem. Soc. A*, 1971, 1777.

25 P. A. W. Dean, D. D. Phillips and L. Polensek, *Can. J. Chem.*, 1981, **59**, 50; P. A. W. Dean, *Can. J. Chem.*, 1983, **61**, 1795.

26 C. Gurnani, A. L. Hector, E. Jager, W. Levason, D. Pugh and G. Reid, *Dalton Trans.*, 2013, **42**, 8364.

27 B. Cordero, V. Gomez, A. E. Platero-Prats, M. Reeves, J. Eschevaria, E. Cremades, F. Barragan and S. Alvarez, *Dalton Trans.*, 2008, 2832.

28 G. E. D. Mullen, P. J. Blower, D. J. Price, A. K. Powell, M. J. Howard and M. J. Went, *Inorg. Chem.*, 2000, **39**, 4093.

29 A. Magistrato, P. Maurer, T. Fassler and U. Rothlisberger, *J. Phys. Chem. A*, 2004, **108**, 2008.

30 A. J. Blake, A. J. Holder, T. I. Hyde, H.-J. Kuppers, M. Schröder, S. Stotzel and K. Weighardt, *J. Chem. Soc., Chem. Commun.*, 1989, 1600.

31 M. J. Hesford, W. Levason, M. L. Matthews and G. Reid, *Dalton Trans.*, 2003, 2852.

32 J. S. Bradshaw, J. Y. Hui, B. L. Haymore, J. J. Christensen and R. M. Izatt, *J. Heterocycl. Chem.*, 1973, **10**, 1; J. S. Bradshaw, J. Y. Hui, Y. Chan, B. L. Haymore, R. M. Izatt and J. J. Christensen, *J. Heterocycl. Chem.*, 1974, **11**, 45.

33 G. M. Sheldrick, *SHELXL-97, Program for refinement of crystal structures*, University of Göttingen, Germany, 1997.

34 G. M. Sheldrick, *SHELXS-97, Program for solution of crystal structures*, University of Göttingen, Germany, 1997.